Novel Russian Technologies for Offgas NOx Reduction

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The U.S. Department of Energy (DOE) has sponsored a series of pilot-scale plasma incineration tests at MSE Technology Applications, Inc. (MSE) under DOE Contract Number DE-AC22-96EW96405 in Butte, MT, during FY97 and FY98 under the DOE's Mixed Waste Focus Area's (MWFA) Controlled Emissions Demonstration (CED) Program. Two sub-tasks under the CED program were to evaluate the performance of new Russian DeNO$_x$ SCR catalysts and the performance of a pulsed corona discharge offgas treatment unit for the removal of high concentration oxides of nitrogen (NO$_x$) from the offgas generated by a plasma arc furnace.

Russian Pulsed Corona Discharge Unit

The Pulsatech™ pollution control technology, developed by Pulsatron, LTD., Los Angeles, Ca. and SEDB Horizont of Moscow, Russia, uses pulsed corona discharge to produce high-energy atoms, molecules, ions, and radicals from O_2, N_2, water vapor, and other offgas components to cause the degradation of gaseous pollutants, such as Nox, Sox, hazardous organics, and gaseous mercury compounds. Gases entering the combustion chamber are energized by electrical pulses from a specially shaped coronating electrode installed coaxially with an outer shell in the reaction chamber. Peak voltage of the pulses is up to 120 kilovolts to ground. The repetition rate of the pulses is 120 hertz with each pulse having a duration of 200 nanoseconds.

Treated pollutants are condensed on the grounding electrode (the steel tube surrounding the coronating electrode) and are removed with water during a washing cycle. This technology is predicted to also remove particulate matter due to the presence of the constant electric field in the through electrode space.

The Pulsatech™ device consists of four vertical stainless steel tubes (reaction chambers that also act as grounding electrodes) and a high voltage central electrode installed within each tube. The overall effect of the pulsed corona discharge in the device is to oxidize contaminants in the gas stream. For instance, NO will be oxidized to an activated nitrogen dioxide or trioxide (NO_2 or NO_3)that will react with available ammonia (NH_3) to form N_2 and water vapor, alternately, ammonia nitrate may form and migrate to the reactor wall. Sulfur compounds in the gas processed in the Pulsatech™ device will be oxidized to sulfuric

acid or ammonia sulphate ($(NH_4)_2\ SO_4$) in the presence of NH_3 in a similar manner. Trace organic compounds will end up as carbon dioxide (CO_2) and water if oxidized completely.

The following were the primary initital test objectives for the Pulsatech™ pollution control device:

- Determine to what extent the Pulsatech™ device can remove NO_x with NH_3 injection.

- Demonstrate the Pulsatech™ pollution control device can destroy 95% of the NO_x generated by the PACT-6 plasma torch with acceptable NH_3 slip (75% reduction of NH_3 injected into the reactor).

Offgas was drawn directly from the primary plasma chamber, pre-filtered and fed into the Pulsatech™ unit at a rate of 2 lb/min at approximately 175° F.

While the Pulsatech™ device was unable to achieve the test objective of 95% removal efficiency for NO_x from the plasma furnace, the NO_x concentrations levels (3,000ppm to 9,000ppm) were higher than the Pulsatech™ design removal rate of 2,000 ppm No_x. Nevertheless, the Pulsatech™ technology was proven successful at removing 80% of the high levels (9,000 ppm) of NO_x with variations in temperature, moisture, NH_3, and O_2 content. The NH_3 slip test objective to not exceed 25% of injected NH_3 levels was met during testing. These conclusions are based on data from January 8, 1998, testing. The equipment supplier believes that a modification to the unit, which would increase the pulses per second from 120 to 800, would allow the unit to remove 95% of the NO_x due to increased average process power.

The unit operated with only one failure during its approximately 23 hours of operation, and this stoppage was caused by a bad solder connection that was easily repaired. The unit was operated remotely for the majority of testing, and operation of the unit is not operator intensive.

Testing is continuing in order to demonstrate the destruction capabilities of the Pulsatech™ device on hazardous organic surrogates. Tests are presently being conducted to test the unit’s ability to destroy toluene, 1-1-1 trichlorethane, benzene, and chloroform.

This technology could possibly be applied to the possible dioxin production issues at the DOE's Consolidated Incinerator Facility at Savannah River, Georgia, or the Waste Experimental Reduction Facility at the Idaho National Environmental Engineering Laboratory (INEEL). It could also possibly be applied to solve

the gaseous mercury problems that are known, suspected, or could exist in future waste treatment campaigns of the four DOE mixed waste thermal treatment facilities, including the Calciner at the INEEL and the Toxic Substance Control Act Incinerator at Oak Ridge National Laboratory.

Russian Catalysts

The objectives of this testing were to compare performance of Russian catalysts with performance of an operating standard catalyst. The ideal Russian catalyst is purported to be environmentally benign (disposable in a regular landfill after useful life) and less expensive.

Three Russian mixed/oxide catalysts (IC-44/I-700, IC-45, and IC-47) developed in FY96 at the Boreskov Institute of Catalysts in Novosibirsk, Russia were tested against a commercially available vanadium and tungsten oxides on a titanium oxide carrier catalyst at various temperatures ranging from 240 to 380 °C, with various ratios of ammonia (NH_3):NO_X (0.8:1 to 1.5:1), and at high inlet NO_X concentrations [from 2,300 to 3,900 ppmv with a nitrogen dioxide (NO_2)/nitric oxide (NO) ratio from 1:50 to 1:4]. The catalysts were tested in a 20 lb/min (262scfm) offgas loop of the Plasma Arc Centrifugal Treatment (PACT-6) system.

Two DeNOx units, a standard MSE catalytic reactor and a smaller slipstream unit containing five Russian catalyst blocks were installed in parallel downstream of the induced-draft stack blower. Flow was split in an approximate 8:1 ratio. In this configuration, the reactor with the Russian catalysts was exposed to approximately the same mass flux as the catalysts in the standard unit. The catalyst carriers were honeycomb-like 7.5 x 7.5 x 15(cm) monoliths with a square cross section normal to flow. The cross-sectional area of the Russian catalyst monolith was approximately one-tenth of the cross-sectional area normal to flow of the standard catalysts. A thermocouple and a sample probe were installed after each of the catalyst stages. The reactor body was insulated to lessen heat loss.

The temperature of the standard catalyst (at the inlet) was typically 50 to 60 °C lower than that of the first stage of the Russian catalyst during the same sweep. The standard reactor typically operates with a gas inlet temperature of approximately 270 °C and conversion of NO_X is typically held at less than 50% and meets the MSE emissions permit. However, the unit is capable of a design conversion rate of more than 95%.

The samples for analysis of NO_2, NO, and NH_3 were taken with

100:1 dilution probes at the combined inlet to both reactors and also at the exit of the first standard catalyst. Each of these samples was analyzed with a dedicated Thermo Environmental Instruments, Inc. analyzer.

The performance of Russian IC-47 catalyst was similar to the performance of a standard catalyst for both NH_3 and NO_X at all conditions. The best results on this catalyst were obtained at a temperature of 372 °C, with a ration of 1:1 NH_3:NO_X, and a NO_X concentration of approximately 3,500 ppmv (3,217 ppmv of NO). The removal efficiency of NO was 95.9%, NO_2 - 96.5%, and the removal efficiency of NH_3 was 88.5%. The total removal efficiency of NO_X was 96%.

The standard catalyst demonstrated 91.9%, 99.3%, and 86.3% for the same nitrogen compounds. Both unused and spent IC-47 catalysts passed the TCLP analysis demonstrating that the catalyst is environmentally benign for the landfill disposal.

The IC-44/I-700 catalyst based on a mixture of zinc, chromium, and iron oxides that have been impregnated with copper performed at approximately 80% to 90% of a standard catalyst, but failed to pass the TCLP analysis for chromium (showing approximately 7.66 milligrams per liter (mg/L), which is above the TCLP limit of 5 mg/L).

The IC-45 catalyst formulation is considered to be the most environmentally benign as compared to the formulations of the other catalysts tested and based on its TCLP analysis results. However, the relative performance of the catalyst was only 40% to 50%.